

Proceedings of the American Academy of Arts and Sciences.

VOL. XXXVIII. No. 15. — DECEMBER, 1902.

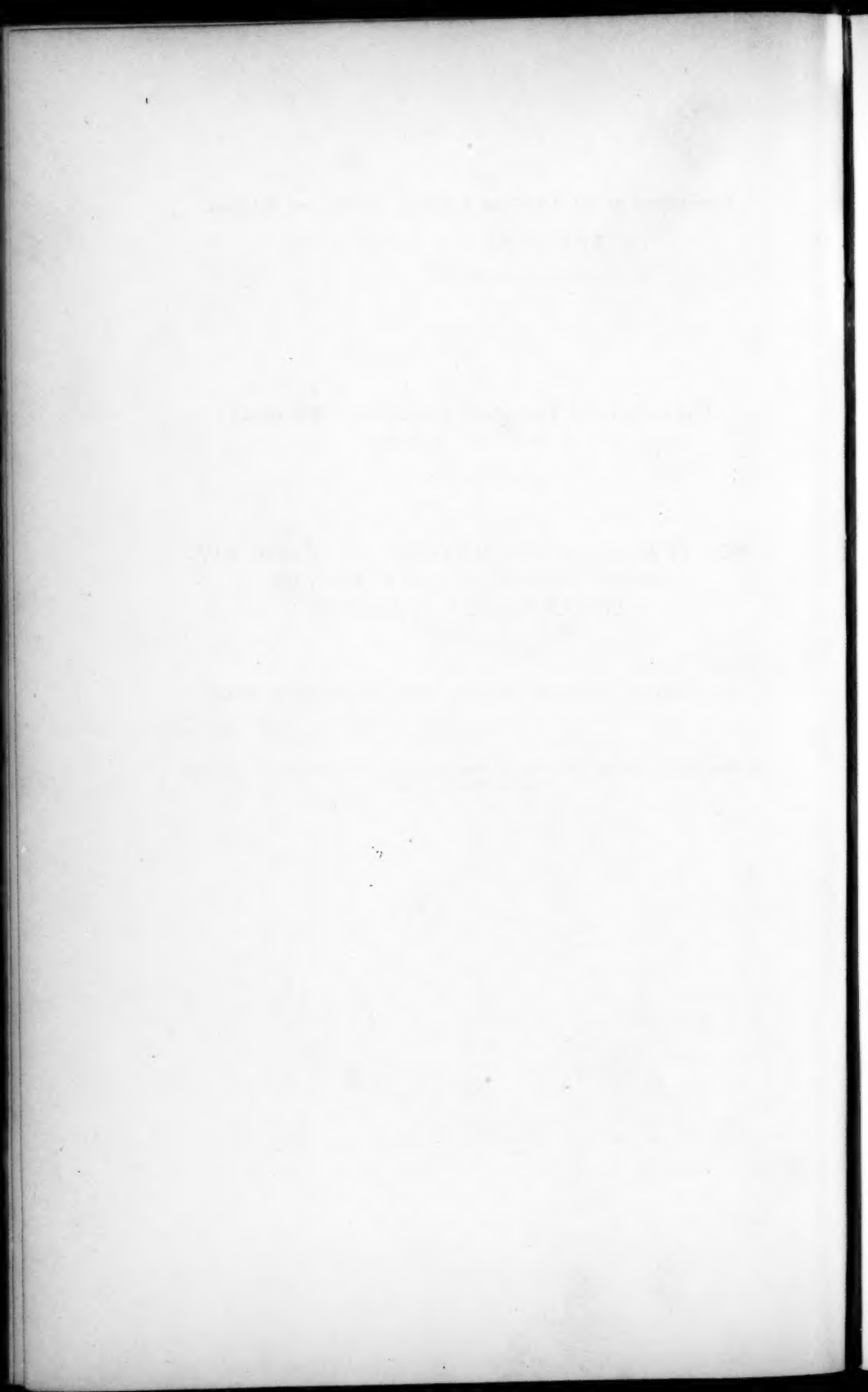
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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY  
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*THE TRANSITION TEMPERATURE OF SODIC SUL-  
PHATE REFERRED ANEW TO THE  
INTERNATIONAL STANDARD.*

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INVESTIGATIONS ON LIGHT AND HEAT, MADE AND PUBLISHED WHOLLY OR IN PART WITH APPROPRIATIONS  
FROM THE RUMFORD FUND.



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Presented November 12. Received October 22, 1902.

In a previous paper\* it was shown that the transition temperature of sodic sulphate serves as a very well defined fixed point in thermometry. The precautions to be observed in its determination were there stated and a preliminary value was given, referring the transition temperature to the international standard. This value was found by means of two accurately standardized Tonnelot thermometers, Nos. 11142 and 11143, kindly loaned by the Jefferson Physical Laboratory; but in order to obtain more certain knowledge of a point so important, obviously more instruments should be used. Furthermore, there was involved an uncertain correction for the column of mercury in the stem, which, owing to the long divisions of the scale, necessarily projected a considerable distance into the air. From final determinations such uncertainty must be eliminated.

This present paper describes a number of determinations wholly independent, although in excellent confirmation of the older results. These new determinations, in the first place, obviate the uncertain correction for the projecting column. Secondly, by means of three new Baudin thermometers acquired by this Laboratory and recently standardized by the International Bureau of Weights and Measures, at Sèvres, the transition temperature is very accurately referred to the international standard.

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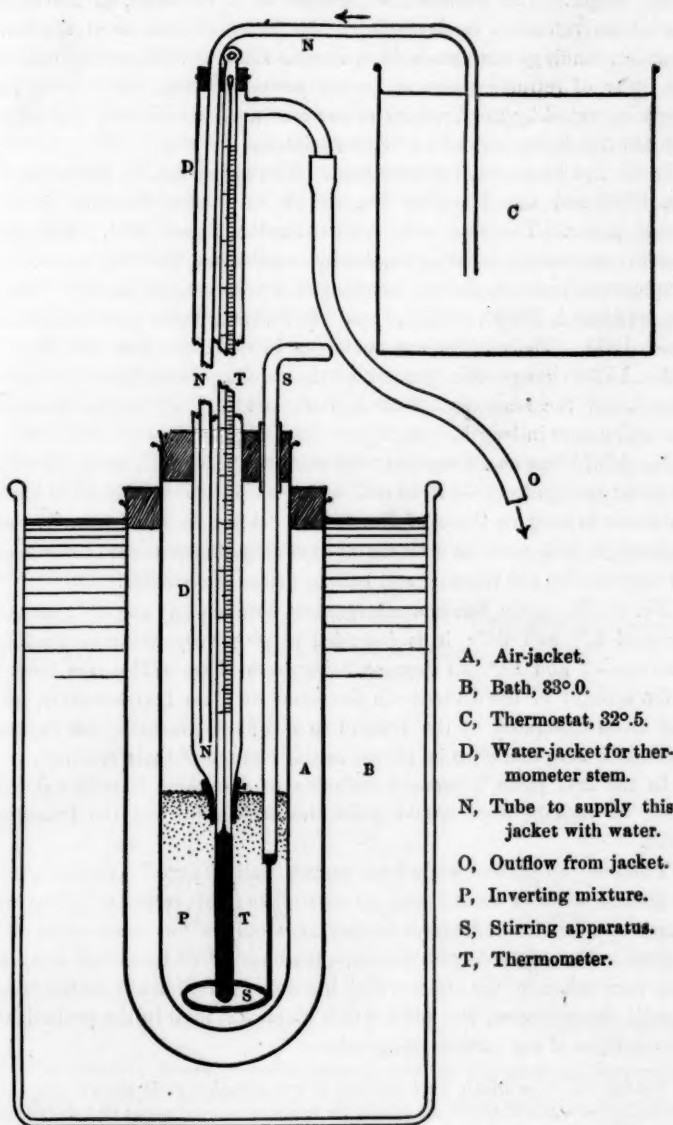
\* Am. J. Sci., [4], 6, 201; Zeit. phys. Chem., 26, 690 (1898).

The general plan of the apparatus used in this work was similar to that described in the previous papers, but there were some modifications in detail. The essential parts of the arrangement are shown in the accompanying figure.

The sodic sulphate was placed in a large test tube in a Beckman freezing-point apparatus. It was found absolutely necessary to surround this test tube by an air-jacket in order to prevent a too sudden inflow of heat, which results in the rapid transition of the hydrated salt and consequent superheating. The outside bath was easily maintained about half a degree above the transition temperature by means of a small platinum resistance coil in the water. The galvanic current used to supply this energy was regulated by an external rheostat. With this arrangement the transition temperature was easily maintained many hours at a time.

As is well known, the true reading of a mercury thermometer is obtained only when the whole stem is the same temperature as the bulb. It was evidently inconvenient to surround the whole stem with sodic sulphate, so the following device was employed. A long tube, of clear glass and even bore, of a diameter about three times as great as the thermometer, was used as a jacket to enclose the thermometer. Through the jacket was kept running a stream of pure water, maintained at a definite temperature by a large thermostat. The water, which entered through a long thin tube parallel with the thermometer, rose through the jacket and flowed out at a side neck at the top. The thermometer bulb emerged from the jacket below through a rubber connection, which was carefully wired with fine platinum wire. In use the jacket almost touched the surface of the sodic sulphate. The diagram facilitates the understanding of the arrangement.

Since the cubic dilation of mercury is 0.000182 and that of hard glass is about 0.000022, the apparent dilation of mercury in glass is about 0.00016. A projecting column thirty-six degrees in length, subjected to a change in temperature of  $0^{\circ}.2$  C., will therefore record a change of  $0^{\circ}.001$  C. in its reading. Since, if possible, we did not wish the error to exceed this amount, the thermostat was not allowed to vary in constancy more than  $0^{\circ}.2$  C., and the thermometer used to record its temperature was itself standardized with sodic sulphate. It should be remarked that in most cases an auxiliary thermometer would be a sufficient guide to the correction for the projecting column since this great degree of accuracy is not often sought. The jacket was used in this particular case in order to make certain of the temperature of the stem throughout its



- A, Air-jacket.
- B, Bath, 33° 0.
- C, Thermostat, 32° 5.
- D, Water-jacket for thermometer stem.
- N, Tube to supply this jacket with water.
- O, Outflow from jacket.
- P, Inverting mixture.
- S, Stirring apparatus.
- T, Thermometer.

whole length.\* To prevent the introduction of an error, on the other hand, from refraction in the glass of the jacket as well as of the thermometer, readings were made from various sides, and the average taken; this error of refraction was of barely perceptible magnitude, and was surely corrected by the diversity of our readings. Great care was taken to place the thermometer in a vertical position.

In all, five thermometers were used. The oldest Baudin thermometer No. 9389 and the Tonnelot No. 11143 have been described in the former paper. The latter was standardized in June, 1894. The new Baudin thermometers were especially constructed for this transition-temperature work, each one including the temperature  $32^{\circ}.38$ . They are numbered 15200, 15275, and 15276, and were standardized in June, 1900. Their bulbs are no larger in diameter than the stem.

No. 15200 has no enlargement of the capillary throughout its entire length, and the scale runs from  $-5^{\circ}$  to  $104^{\circ}$ . Each degree is about six millimeters in length.

No. 15275 has an enlargement between  $+2^{\circ}$  and  $30^{\circ}$ , being intended to give readings from  $-11^{\circ}$  to  $+2^{\circ}$  and from  $30^{\circ}$  to  $112^{\circ}$ . Its degrees are about as long as those of No. 15200. After its use in the present research, it will serve as a means of verifying thermometers to be used for determining the freezing and boiling points of solutions.

No. 15276, lastly, has one enlargement between  $38^{\circ}$  and  $65^{\circ}$ , another between  $67^{\circ}$  and  $98^{\circ}$ ; it is intended to give very accurate readings between  $-2$  and  $38^{\circ}$ , its degrees being each eight millimeters long.

On account of the diversity in the forms of these thermometers, each had to be calibrated by the Bureau in a different fashion, and especial confidence may therefore be placed in the average of their readings.

In the first place it seemed desirable to determine if sodic sulphate made in various ways would yield the same value for the transition point.

The first sample was made from commercially "pure" Glauber's salt. A filtered solution was allowed to crystallize; this recrystallization was found to raise the transition temperature only a few hundredths of a degree. After five recrystallizations, readings of its transition temperature were taken on the old sensitive but only approximately standardized Baudin thermometer, No. 9389, which alone was used in the preliminary comparisons of the various preparations.

\* After the experiments were finished, it was found that in spite of the rapid circulation of water through the jacket, its temperature was about  $0^{\circ}.4$  lower than that in the thermostat. Hence a correction of  $0^{\circ}.002$  must be added to the final result.

The second sample of sodic sulphate was made by neutralizing with sulphuric acid a quantity of sodic bicarbonate, which had been well washed with cold water. The product thus obtained was recrystallized many times, and readings taken as recorded below.

Sample III was later made from the filtrates of the various recrystallizations, and sample IV was made from a mixture of I and II when they became too small in amount to recrystallize separately.

It was convenient in this preliminary work to take successive readings of the transition temperature of several samples of salt, and then to take the reading of the thermometer in melting ice. In all cases except the first two, the lower fixed point was determined immediately after the upper one. Since commercial ice was found to contain impurity enough to change its melting point by several thousandths of a degree, pure ice was made for the zero observations. The purest water, twice redistilled, was frozen in platinum. After using some ice thus prepared it was found that 100 grams of the resulting water gave, on evaporation, a residue of only 0.0006 gram, the effect of which on the freezing point would be negligible in this work even if it had all consisted of sodic chloride.

The results of these measurements, recorded in terms of the hydrogen scale, were as follows :

Sample.			Temperature of Transition.
(1)	I,	5th recrystallization	32.376°
(2)	I,	6th "	32.372°
(3)	II,	6th "	32.376°
(4)	II,	7th "	32.384°
(5)	II,	8th "	32.380°
(6)	II,	8th "	32.380°
(7)	III,	1st "	32.376°
(8)	III,	2d "	32.383°
(9)	III,	3d "	32.376°
(10)	IV,	1st "	32.389°
(11)	IV,	2d "	32.376°
Average . . . . .			32.379° ± 0.001

In the previous communication already quoted, this same thermometer is reported to have given as the transition of sodic sulphate the value 32.482 in mercurial degrees, or 32°.378 on the hydrogen basis. Thus it



is clear that the newly made sodic sulphate is identical with that prepared in 1898; and since the most serious deviation to be observed above is seen in the two determinations of the purest sample (No. IV) it is evident that the slight irregularities are to be ascribed rather to the difficulties of thermometry than to any fault of the preparations.

The preliminary values with this one thermometer having thus proved that the salt made by different methods gives identical results within the limit of error of the experiment, readings were taken with the more accurate thermometers.

In the final work, all the precautions mentioned by Guillaume to be observed in using thermometers were adhered to as closely as possible.\*

Inasmuch as it was not convenient to make large quantities of pure ice where it was desired to make only one reading at a time, we preferred to make our ice readings in a tube similar to that used for the sodic sulphate; but the tube was always well filled with the pure ice and the requisite volume of purest cold water and then surrounded with a large jar of ordinary ice. The thermometer, in a vertical position, was read with an accurate Geneva cathetometer.

The purest sodic sulphate, as obtained by the methods given above, was used. It was found that a slight efflorescence was amply sufficient to supply the anhydrous phase of the sodic sulphate. The average specific gravity of the inverting mixture was found to be about 1.5.

Besides the barometric pressure, the depth of immersion of the thermometer in the solution was always noted in order to correct for external pressure.

The complete record of an observation is given below in order to show the manner of applying the corrections: † —

No. 15, March 7, 1901.

Baudin, 15200.

Corrected Barometer	766.3 mm.	766.3 mm.
59 mm. pressure of salt	6.6	
" " of water		4.3
	<u>773.9 mm.</u>	<u>770.6 mm.</u>

\* Guillaume, *Traité pratique de la Thermométrie de Précision* (1889).

† See "Notice sur les Thermomètres à mercure," Paris, Gauthier-Villars et Fils, 1896. This paper accompanies the thermometers.



Reading in salt	32.486°	in ice .054°
Correction, calibration	— .002	.000
“ exterior pressure	— .002	— .001
“ interior “	+ .039	+ .009
Corrected reading in ice	<u>— .062</u>	<u>.062°</u>
	32.459°	
Correction, fundamental interval	<u>+ .023</u>	
	32.482°	
Correction, hydrogen scale	<u>— .104</u>	
	32.378°	

Eleven such observations were made, with the help of four very accurately standardized thermometers of the finest possible workmanship. Since the salt was essentially the same in each case, these are grouped below according to the instruments. The question no longer concerns the accuracy of the temperature, but it concerns rather the accuracy of the several thermometers. If they can be shown to be in substantial agreement, the certainty of the reference to the international standard will be correspondingly assured.

## FINAL DETERMINATIONS.

## (HYDROGEN STANDARD.)

Baudin 15200	(12)	32.379°	
	(13)	32.380°	
	(14)	32.377°	
	(15)	<u>32.378°</u>	Average, 32.379°
Baudin 15275	(16)	32.385°	
	(17)	<u>32.386°</u>	Average, 32.385°
Baudin 15276	(18)	32.378°	
	(19)	<u>32.376°</u>	Average, 32.377°
Tonnelot 11143	(20)	32.380°	
	(21)	32.381°	
	(22)	<u>32.386°</u>	Average, 32.382°
Total Average . . . . .		32.381°	
Correction (footnote, p. 434) . . . . .		<u>+0.002</u>	
Final result . . . . .		32.383°	

It will be seen that the maximum variation of any minor average from the total average is only  $0^{\circ}.004$ . The Tonnelot thermometer, standardized by the Bureau Internationale des Poids et Mesures in 1894, gives essentially the same result as the average of the three new thermometers — a result which indicates in the clearest manner the excellent quality of the work of the Bureau. The final result,  $32^{\circ}.383$ , is only  $0^{\circ}.004$  higher than the value found by one of us in 1898 — a difference about equal to the average deviation of the older experiments from their mean. If each experiment of the recent series is taken as of equal weight, the “probable error” — of the total average is  $0^{\circ}.0007$ ; while if each minor average is considered as an observation, the “probable error” becomes  $0^{\circ}.001$ . These very small figures indicate that further multiplication of observations is needless. The transition temperature of sodic sulphate has been determined in terms of the international standard to within the limit of accuracy of the standard itself.

Before closing this report, it is perhaps worth while to emphasize in comparison the possible uncertainties of the three fixed points in the thermometric scale, —  $0^{\circ}$ ,  $32.383^{\circ}$ , and  $100^{\circ}$ .

The freezing point of water (an equilibrium of two phases) is dependent upon three essential conditions: first, the pressure; secondly, the purity of the water; thirdly, the homogeneity of the crystal form of the ice.

It is well known both theoretically and practically, that pressure lowers the melting point of ice, because this substance is more voluminous than water. The temperature chosen for the international standard of thermometry is not the true triple point of the substance, but a point  $0^{\circ}.007$  lower, — the freezing point under atmospheric pressure. Ordinary variations in this pressure cause an effect on the temperature smaller than the necessary errors of observation; hence the effect of changing atmospheric pressure may be disregarded, as well as the effect of the pressure of a few centimeters of liquid above the thermometer bulb.

The second possible cause of deviation, impurity in the water, causing a lower freezing point because of its osmotic pressure, is easily avoided. Water is more easily purified than almost any other substance, and even commercial ice often approximates the required purity within a few thousandths of a degree. Attention should be called, however, to the danger of dissolving volatile impurities from the atmosphere. This danger is much less when the interstices between the pieces of ice are wholly filled with pure water; and it is obviously well to add water which has been boiled in a platinum or silver flask and rapidly cooled,

rather than to wait for the ice to supply the needed liquid by melting. Marek\* has shown that pure ice after being rinsed and drained may indicate a freezing point as much as  $0^{\circ}.016$  too low; and six carefully conducted experiments of our own indicated almost as great an error from this source ( $0^{\circ}.008$ ). It is almost needless to state that in the final experiments above the ice was properly mixed with the purest water.

The third cause of irregularity in the melting point of ice is not so frequently considered. Nichols† has shown that the specific gravity of ice may vary from 0.9161 to 0.9180, according to circumstances; and it is hardly conceivable that such varieties could give identical melting points. It may be that after a skeleton of freely forming crystals has been built, the interstices between the crystals are filled with a less compact structure.‡ Tyndall's well known experiment on the "flowers of ice" seems to support this conclusion. Marek has shown that even the strains produced in cracking the ice may cause serious errors, unless much water is present. In our own experiments, as already stated, the ice was made by freezing the purest boiled water in a platinum dish, and was wholly clear and devoid of apparent crystalline structure. The pressure under which the ice was formed was essentially the atmospheric pressure, the layer of liquid being shallow, and the ice was easily broken.

The transition temperature of sodic sulphate, a quadruple point, compares favorably with this long established fixed point, in every respect. The volume changes so little during the transition that even the pressure of an atmosphere produces no perceptible effect on the temperature,§ the purity of the substance is quite as easily obtained as that of water, and the certainty of definite crystalline form and consequent homogeneity is probably greater, because the habit of growth causes many independent freely growing crystals, rather than a commingled heterogeneous mass. The somewhat lower "latent heat of melting" is not a serious drawback if reasonable precautions are taken to prevent the inflow of heat from outside.

The third constant point,  $100^{\circ}$ , involves pressure and the purity of substance, like the others; but since no solid enters into the question, the doubt as to homogeneity is eliminated. To neutralize this advantage, two disadvantages appear; first the danger of superheating the vapor;

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\* Guillaume, *Traité*, p. 118.

† Nichols, *Phys. Rev.*, **8**, 21 (1899); *Z. phys. Chem.*, **36**, 240.

‡ See also Pernet, Guillaume's *Traité*, p. 118.

§ Dr. G. N. Lewis has found in this Laboratory that the volume change is not over 0.5 per cent.

and secondly the necessity of knowing the pressure with the greater precision, since the tenth of a millimeter changes the boiling point by  $0^{\circ}.004$ . Hence, without a barometer of the best construction, and many precautions, one can hardly hope to attain a result accurate to within  $0.01^{\circ}$ .

The causes of error in the three fixed points just mentioned are inherent in the nature of the equilibria, and to these must be added those dependent upon the method of thermometry. The behavior of the liquid mercury, usually used to indicate temperature, leaves little to be desired; but as is well known, the glass receptacle is far less satisfactory. Its sluggish expansion and contraction may easily introduce errors of a degree or more at high temperatures, and the effect of this cause of error becomes the more important as the temperature-interval increases. Even at  $100^{\circ}$  serious mistakes may thus result. Hence it is important to choose as a standard some temperature as near as possible to the temperature read. In this respect  $32^{\circ}.383$  is far superior to either of the usually accepted standards, because most temperature measurements lie in the neighborhood of  $20^{\circ}$ .

The careful study of the transition temperatures of other salts has been continued, and while it has led to results which may be of subsidiary importance, no salt has been found which seems to be as generally useful as sodic sulphate. Hence we unhesitatingly recommend this substance as providing one of the most convenient means known for attaining a precisely definite temperature. It has even been used in this Laboratory with success on a large scale in a bath containing over ten kilograms; the description of this undertaking will be found in the preceding paper.

The writers are much indebted to the Rumford Fund of the American Academy for pecuniary assistance in this investigation.

#### SUMMARY.

The present paper contains the record of experiments which verify in a satisfactory manner the earlier estimate of the transition temperature of sodic sulphate. Its exact place on the international hydrogen scale is found to be  $32^{\circ}.383 \pm 0.001$ , by means of four thermometers standardized by the Bureau International des Poids et Mesures. It is recommended as being at least as trustworthy as the other two fixed points used for defining temperature, and is possibly the most generally useful of the three.

CAMBRIDGE, MASS., 1900-1902.